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PCL Makro Başlatıcı Kullanarak ATRP ve ROP ile Blok Kopolimerlerin Tek Basamakta Sentezi

Sema ALLI[1*]

ÖZET: Poli(laktid)-b-poli(ε-kaprolakton)-b-poli(stiren) üç bloklu kopolimerler atom transfer radikal polimerizasyonu ve halka açılma polimerizasyonuyla aynı anda bir basamakta tek kap yöntemiyle sentezlendi. İlk olarak, ε-kaprolakton'nun (ε-CL) kalay (II) 2-etilheksanoat katalizörü varlığında 110 °C'de halka açılma polimerizasyonuyla PCL sentezlenip, ardından 2-bromopropiyonil bromür ile esterleşmesi sonucu bromlanmış poli(ε-kaprolakton) (PCL-Br) makro başlatıcı olarak hazırlanmıştır. Tek kap yöntemiyle, stiren (St) monomerinin PCL-Br makro başlatıcısıyla CuCl/PMDETA sistemi varlığında [I]:[CuCl]:[PMDETA]=1:1:3 mol oranları kullanılarak, 120 °C'de toluen içinde ATRP'si ile ve D, L laktidin HAP'nu aynı anda gerçekleşti. Böylece, kontrollü molekül ağırlıklarına ve orta derecede dar polidispersitelere sahip blok kopolimerler elde edildi. Tek kap polimerizasyonunu etkileyen monomer konsantrasyonu, başlatıcı konsantrasyonu ve polimerizasyon süresi gibi temel parametreler araştırıldı. Elde edilen polimerler, ^{1}H NMR, FTIR ve GPC teknikleri kullanılarak karakterize edildi.

Anahtar Kelimeler: D, L-laktid, ε-kaprolakton, stiren, atom transfer radikal polimerizasyonu, halka açılma polimerizasyonu

One-Pot Synthesis of Block Copolymers via ATRP and ROP Using PCL Macroinitiator

ABSTRACT: Poly(lactide)-b-poly(ε-caprolactone)-b-poly(styrene) triblock copolymers were synthesized simultaneously by one-pot method using atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) in one step. Firstly, brominated poly(ε-caprolactone) (PCL-Br) as macroinitiator was made via ROP of ε-caprolactone (ε-CL) in the existence of tin(II) 2-ethyl hexanoate at 110 °C followed by esterification with 2-bromopropionyl bromide. With the one-pot method, the simultaneously via ROP of D, L-lactide in the existence of tin(II) 2-ethyl hexanoate and ATRP of styrene (St) monomer with PCL-Br macroinitiator in the presence of CuCl/PMDETA system using [I]: [CuCl]:[PMDETA]=1:1:3 molar ratios at 120 °C in toluene was performed. Thus, the block copolymers with controlled molecular weights and moderately narrow polydispersities were obtained. Principal parameters, such as monomer concentration, initiator concentration, and polymerization time, which effect the one-pot polymerization were investigated. The polymers obtained were characterized using ^{1}H NMR, FTIR, and GPC technique.

Keywords: D, L-lactide, ε-caprolactone, styrene, atom transfer radical polymerization, ring-opening polymerization

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INTRODUCTION

Researchers have received considerable interest in ABC triblock copolymers and their synthesis, as well as their various morphological structures and possible applications (Ma et al., 2009; Palacios et al., 2017; Huang et al., 2018). Today, there are a wide variety of living/controlled polymerization techniques to obtain ABC triblock copolymers of various structures, solubility and functionality by sequential polymerization of various monomers. These techniques of polymerization include “living” radical polymerizations and “living” ionic polymerisations (Davis and Matyjaszewski, 2001; Jiang et al., 2006). In addition, ABC triblock copolymers are synthesized by combining them with various methods (Luan et al., 2004; Mahajan et al., 2004).

To synthesize macromolecules with the demanded morphology and molecular weight, controlled radical polymerization (CRP) techniques such as reversible addition-fragmentation chain transfer (RAFT) polymerization (Moad et al., 2005; Şanal et al., 2015), atom transfer radical polymerization (ATRP) (J. S. Wang and Matyjaszewski, 1995; Haddleton et al., 1997; 2005; Lee et al., 2005), and nitroxide-mediated polymerization can be used (Hawker et al., 2001; Benoit and Maric, 2008; Allı et al., 2016). When compared to other CRPs, ATRP has a number of advantages. ATRP provides a general and effective method of polymerization of a wide variety of monomers with different chemical functionalities, don’t need harsh conditions and is tolerant of functional groups and impurities (J. S. Wang and Matyjaszewski, 1995; He et al., 2007).

A one-pot method for synthesizing block or graft-shaped copolymers was successfully used using diverse methods, and it has many advantages over other widely used methods (Villarroya et al., 2006; Yu et al., 2012; Allı et al., 2014; Yilmaz, 2019). Since at least two conversion steps can be applied synchronous, side reactions that cause the creation of homopolymers are decreased. The use of ring-opening polymerization (ROP) and controlled radical polymerization (CRP) simultaneously for block polymers with structures made of biodegradable aliphatic polyesters and polyacrylate has recently been shown in the literature to be an effective strategy for block polymers with structures made of both. For example, partially biodegradable and biocompatible PLA-b-PHEMA block copolymers were synthesized by the combining of ROP and ATRP using a difunctional initiator (Wolf et al., 2009). PLLA-b-PMMA polymers were synthesized in a single step using a bifunctional initiator via ATRP with UV light and ring-opening polymerization methods simultaneously (Lei et al., 2018).

Moreover, using a combining of the ROP and ATRP polymerization methods have been reported the synthesis of many copolymers containing styrene (Aydogan et al., 2017), methyl acrylate (Choochottiros et al., 2012), methyl methacrylate (Ydens et al., 2003; Choochottiros et al., 2012) , 2-(dimethylamino)ethyl methacrylate (Xie et al., 2008), 2-hydroxyethyl methacrylate (Wolf et al., 2009), N-isopropylacrylamide (Liu et al., 2015), ε-caprolactone (Deng et al., 2007; Yilmaz, 2019) and lactide (Messman et al., 2005; Kryuchkov et al., 2014; Lei et al., 2018). Lactide and ε-caprolactone homopolymers and copolymers are particularly interesting among aliphatic polyesters because of their medical applications (Keefe et al., 2001; Ko and Lin, 2001; Broström et al., 2004; Sivalingam et al., 2004). These polymers have been widely used for biodegradable sutures, drug delivery systems, temporary scaffolding for tissue, and implantable screws (Li et al., 2003; C. Wang and Hsiue, 2005; F. Wang et al., 2008). However, these polymers have a difficult time undergoing controlled degradation due to their high crystallinity. As a consequence, the properties and architecture of these biodegradable polyesters must be altered. Due to their distinct structures and properties, aliphatic polyesters with well-defined structures, such as comblike polymers (Breitenbach et al., 2000), hyperbranched polymers (Zhai et al., 2003; Nartop et al., 2019: Hasanoğlu et al., 2021), star polymers (Finne and

Albertsson, 2002; J. L. Wang et al., 2005), and dendrimers (Cordova et al., 1998; Persson et al., 2006; Hasanoğlu and Sarı, 2020) are attracting interest.

In this study, The PCL-b-PSt block copolymer is made by initiating ATRP of styrene with a PCL-Br, which is made by esterifying 2-bromopropanoyl bromide and PCL. A series of block copolymers of PLA-b-PCL-b-PSt were polymerized using the PCL-Br macroinitiator by combining ATRP and ROP.

MATERIALS AND METHODS

Materials

ε-Caprolactone (CL, Aldrich, 97%) was vacuum distilled over calcium hydride. Styrene (St, 99%, contains 250 ppm 4-tert-butylcatechol (TBC) as inhibitor) was supplied by Aldrich, which was passed through a short column of basic alumina in order to remove TBC inhibitor prior to use. D, L-lactide (3,6-Dimethyl-1,4-dioxane-2,5-dione) was supplied from Aldrich and used as received. Tin (II) 2-ethyl hexanoate ($Sn(Oct)_2$, triethylamine (TEA), Pentamethyldiethylenetriamine (PMDETA), CuCl, 2-bromopropionyl bromide, and diethanolamine were procured from Sigma-Aldrich. CuCl (98%) was purified by stirring overnight in acetic acid. All other reagents and solvents were obtained at the highest purity available from Aldrich and used as received unless stated otherwise.

Characterization Methods

Proton nuclear magnetic resonance (^{1}H NMR) measurements were recorded using a Bruker 400 MHz NMR spectrometer with chloroform-d as the solvent. Fourier-transform infrared (FTIR) spectra were collected using the IR Prestige 21 model FTIR and Shimadzu FTIR Spectrometer 100. The FTIR spectra were measured as KBr samples of the block copolymers. The EcoSEC HLC-8320 SEC system fitted with a UV (254 nm) and refractive index (RI) detector was used to carry out molecular sieve (size-exclusion) chromatography (SEC) measurements. Calibration was performed by Polymer Laboratories using poly(styrene) standards. Tetrahydrofuran (THF) was used at at 40 ^{o}C and a flow rate of 0.6 mL/min as an eluent.

Preparation of PCL-Br Macroinitiator

Poly (ε-caprolactone) was synthesized via the ROP of ε-caprolactone and $Sn(Oct)_2$ as the catalyst. A 0.02 g $Sn(Oct)_2$ was charged to a 100 mL dry schlenk tube fitted with a magnetic bar in a standard experiment under a dry argon atmosphere. Then, using a dry syringe, 25.50 mL CL was injected.The flask had been immersed in an oil bath preheated to 110°C for a period of 1 hour.The reaction mixture was dissolved after 1 hour by the addition of 100 mL THF and 600 mL petroleum ether precipitated, finally dried under vacuum at room temperature 24 hours. PCL was used for the synthesis of the brominated poly(ε-caprolactone) (PCL-Br). Esterification of end hydroxyl groups PCL with 2-bromopropionyl bromide was achieved based on the reported procedure (Allı et al., 2012).

Synthesis of PCL-b-PSt by ATRP

PCL-b-PSt block copolymer was obtained by ATRP. The standard polymerization method was as follows: 0.50 g (0.065 mmol) of PCL-Br and 6.39 mg (0.065 mmol) of CuCI were poured into a flame-dried Schlenk flask equipped with a magnetic stirring bar. Then, under an argon atmosphere, 1.39 g of styrene, 2 mL of toluene, and 0.0135 mL (0.195 mmol) of PMDETA were inserted into the Schlenk flask with a syringe.The flask was placed in a heated oil bath at 80 ° C for 5 h under argon. After cooling to room temperature, the reaction mixture was passed through neutral silica gel, and the solvent was extracted using a rotary evaporator. The obtained polymer was dissolved in dichloromethane and precipitate into extremely cold methanol. It was then dried under a vacuum at 40 °C until it reached constant weight.

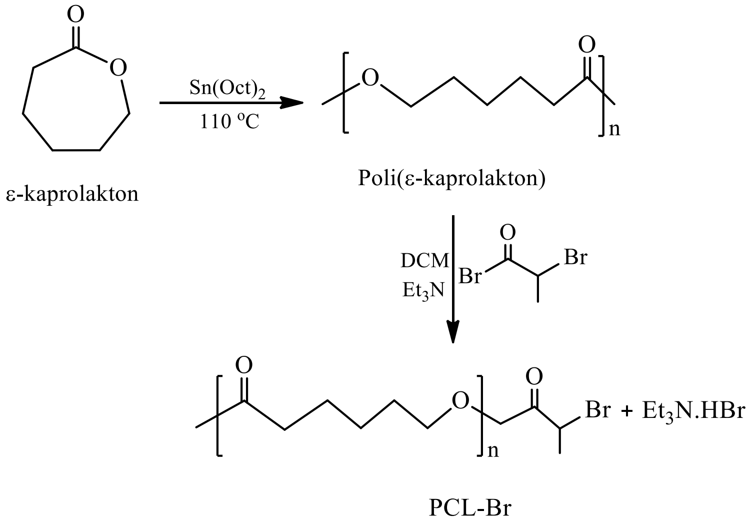
One-Pot Synthesis of PLA-b-PCL-b-PSt Block Copolymers

The standard polymerization method was as follows: 1.00 g of PCL-Br, 0.01 g Sn(Oct)$_2$ and 0.066 g CuCI were filled into a flame-dried Schlenk flask fitted with a magnetic stirring bar. Then 1.00 g of D, L-Lactide, 1.18 g of styrene, 2 mL of toluene and 0.042 mL of PMDETA were injected into the Schlenk flask by a syringe under argon atmosphere. The flask was placed into an oil bath preheated at 120 °C for 5h under argon. Other conditions are shown as follows: The feed ratio was $[M_0]:[I_0]:[CuCl]:[PMDETA]=[100]:[1]:[1]:[3]$. After the polymerization, the reaction mixture was passed through a neutral silica-gel column after cooling to room temperature, and the solvent was collected using a rotary evaporator. The obtained polymer was dissolved in dichloromethane and precipitate into extremely cold methanol. It was then dried under a vacuum at 40 °C until it reached constant weight.

RESULTS AND DISCUSSION

Synthesis of PCL-Br Macroinitiator

Poly(ε-caprolactone) (PCL) was synthesized with caprolactone in the existence of tin(II) 2-ethyl hexanoate via ring-opening polymerization for 1 hour in bulk at 110 ^{o}C and the molar mass of 3310 (Mn) Da (PDI=1.67) was obtained in 85% yield . The bromine terminated poly(ε-caprolactone) (PCL-Br) of 3740 (Mn) Da (PDI=1.74) was synthesized from the esterification reaction of PCL with 2-bromopropanoyl bromide (Scheme 1).^{1}H NMR spectra of the PCL and PCL-Br macroinitiator have been shown in Figure 1 which confirmed the chemical structures indicating the characteristic signals: δ (ppm), signals at 4.05 ppm (–C**H$_2$**–O–), 2.40 ppm (-C**H$_2$**-C=O), and 1.40 ppm (-C**H$_2$**-) for Poly(ε-caprolactone); after the reaction with 2-bromopropanoyl bromide and then appeared a new signal at 4.41- 4.38 ppm for –(CH$_3$)-C**H**-Br for PCL-Br macroinitiator.



Scheme 1. Reaction design of bromine terminated Poly(ε-caprolactone)

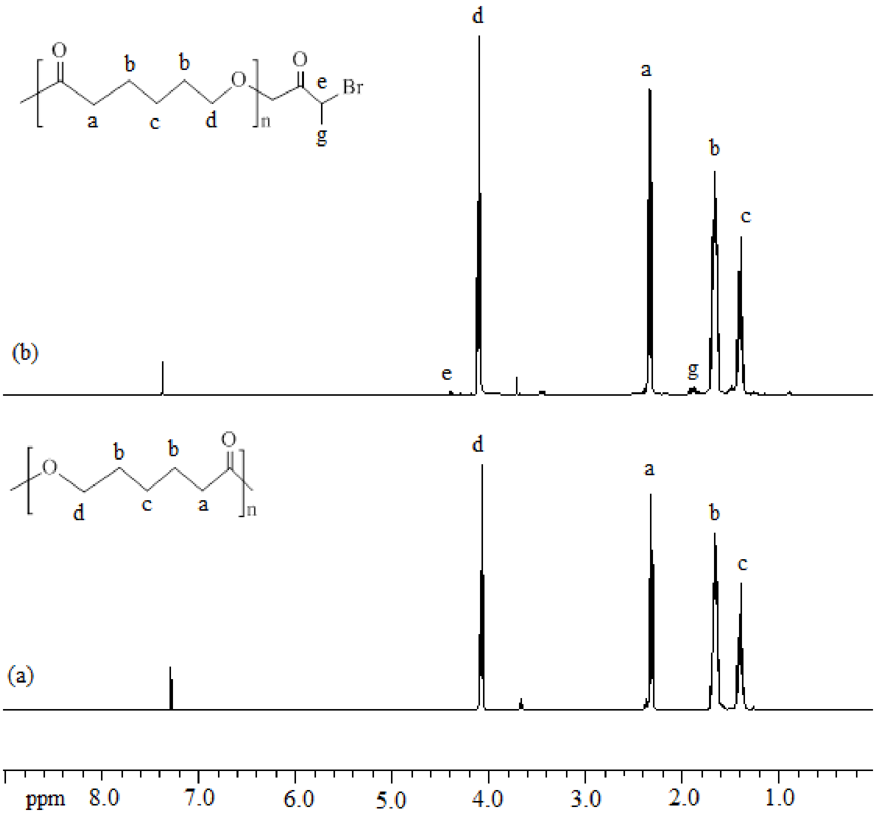
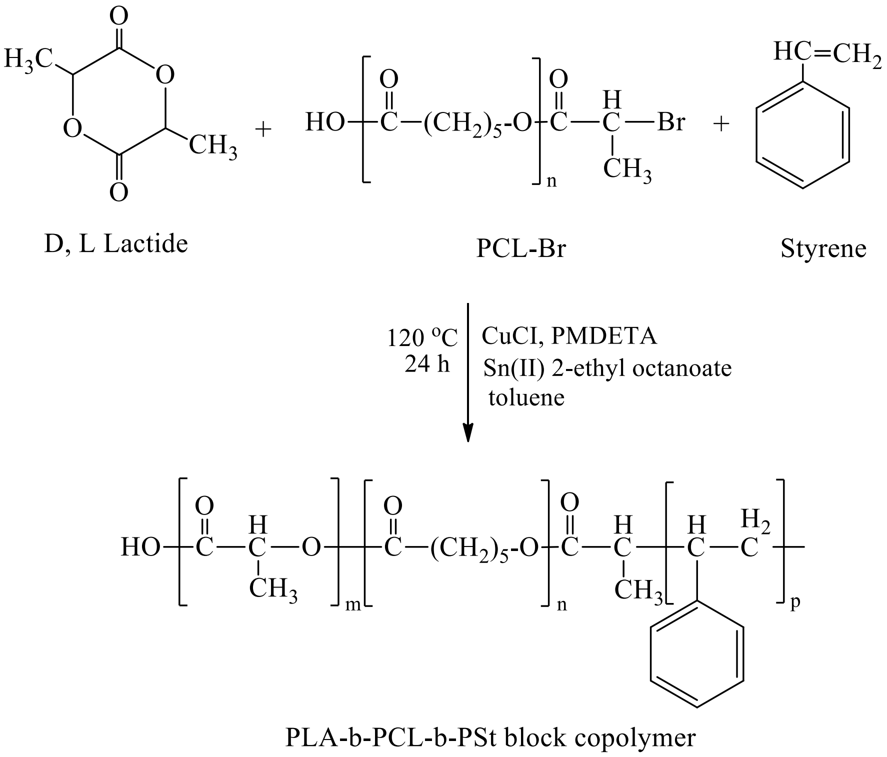


Figure 1. ^{1}H NMR spectra of Poly(ε-caprolactone) (a); PCL-Br macroinitiator (b)

Synthesis of Triblock Copolymers from PCL-Br Macroinitiator

Triblock copolymers were obtained in the one-pot. The ATRP-ROP macroinitiator (PCL-Br) initiates a one-pot polymerization of a lactone and a vinyl monomer in Scheme 2. Ring-opening polymerization of D, L-lactide and atom transfer polymerization of styrene were carried out simultaneously to obtain the triblock copolymers. PLA-b-PCL-b-PSt block copolymers were produced from a styrene and lactide combination that was started by the PCL-Br macroinitiator in the presence of CuCI/PMDETA as an ATRP catalyst and tin(II) 2-ethyl hexanoate as a ring-opening catalyst. Simultaneous ATRP and ROP processes in one-pot were used to research the impacts of initiator and monomer concentrations and polymerization time on copolymerization using PCL-Br macroinitiator. Tables 1, 2, 3, and 4 show the results obtained.

The effect of styrene concentration on PLA-b-PCL-b-PSt block copolymers polymerization in one-pot. The results of PCL-b-PSt and PLA-b-PCL-b-PSt block copolymers are shown in Table 1. As the quantity of styrene increased, the product and molar mass of the block copolymers increased as predicted. The PCL-b-PSt block copolymer has a molar mass of 8920 Da (Mn), while the PLA-b-PCL-b-PSt three block copolymers have molar masses ranging from 10220 Da to 15030 Da (Mn). ^{1}H NMR was also used to calculate the weight percentages of each block in the block copolymer structure. In PCL-b-PSt (PCLSt) block copolymers, the ratio of PCL is found to be 89.13 percent. According to the quantity of styrene inserted, the percentage of polystyrene (PSt) in the triblock copolymer raised. The percentage of the quantity of PSt is found to be 10.08 % PCLLaSt-1, 15.35 % in PCLLaSt-2, 25.10 % in PCLLaSt-3, and 44.11% in PCLLaSt-4, respectively.



Scheme 2. Reaction design of PLA-b-PCL-b-PSt block copolymers

Table 1. The impact of increasing the quantity of styrene on one-pot block copolymerization

Code	St (g)	Yield (wt%)	PCL* (wt%)	PSt* (wt%)	PLA* (wt%)	Mn,GPC (kDa)	Mw,GPC (kDa)	PDI
PCLSt[a]	1.35	20.63	89.13	10.87	-	8.92	12.27	1.38
PCLLaSt-1	1.18	67.30	37.48	10.08	42.44	10.22	15.57	1.52
PCLLaSt-2	1.39	75.47	53.32	15.35	31.33	12.25	18.55	1.47
PCLLaSt-3	2.08	85.30	38.85	25.10	36.06	13.44	21.39	1.59
PCLLaSt-4	2.78	90.38	31.04	44.11	24.87	15.03	24.05	1.60

*Calculated from ^{1}H NMR . [a]ATRP of PCL-Br with styrene at 80 ºC for 5 h; PCL-Br: 0.50 g. PCL-Br: 1.00 g; LA: 1.00 g.

The impact of increasing the quantity of PCL-Br macroinitiator on one-pot block copolymerization is shown in Table 2. The increasing quantity of resulted in an expected decrease in the product and molar mass of the block copolymers. The molar masses of PLA-b-PCL-b-PSt block copolymers have ranged from 15160 Da to 8630 Da (Mn) as shown in Table 2. The addition of more PCL-Br macroinitiator to the reaction mixture results in the production of more active centres. As the number of macroinitiator increases, the molecular weight of the block copolymers decreases, resulting in shorter PSt and PLA units of the obtained block copolymers. Similar situations have been presented in the literature (Öztürk et al., 2010; Allı et al., 2014; Öztürk et al., 2016).

Table 3 shows the impact of increasing the quantity of D, L-lactide (LA) on one-pot block copolymerization. As the quantity of LA increased, the production and molar mass of the block copolymers increased as well. In the one-pot block copolymerization of increasing the amount of LA, molar masses increased from 12250 Da to 14700 Da (Mn) as shown in Table 3. ^{1}H NMR was also used to calculate the weight percentages of each block in the block copolymer structure. The percentage of LA in the triblock copolymer increased according to the quantity of added LA. The percentages of PLA found to be %31.33 PCLStLa-1, % 51.60 PCLStLa-2, % 63.47 PCLStLa-3, and % 72.50 PCLStLa-4, respectively.

Table 2. The impact of increasing the quantity of PCL-Br macroinitiator on one-pot block copolymerization

Code	PCL-Br (g)	Yield (wt%)	PCL* (wt%)	PSt* (wt%)	PLA* (wt%)	Mn,$_{GPC}$ (kDa)	Mw,$_{GPC}$ (kDa)	PDI
PLaStCL-1	0.50	76.7	28.84	10.05	61.11	15.16	19.49	1.52
PLaStCL-2	1.00	74.4	38.65	11.38	39.97	10.02	15.17	1.62
PLaStCL-3	2.00	67.5	47.47	19.76	33.77	9.28	14.99	1.61
PLaStCL-4	3.00	46.0	51.65	21.57	26.78	8.63	14.15	1.63

*Calculated from ^{1}H NMR. St: 1.00 g; LA: 1.00 g

Table 3. The impact of increasing the quantity of D, L-lactide (LA) on one-pot block copolymerization

Code	LA (g)	Yield (wt%)	PCL* (wt%)	PSt* (wt%)	PLA* (wt%)	Mn,$_{GPC}$ (kDa)	Mw,$_{GPC}$ (kDa)	PDI
PCLStLa-1	1.00	75.47	53.32	15.35	31.33	12.25	18.55	1.47
PCLStLa-2	2.00	81.03	19.04	29.36	51.60	12.37	19.58	1.58
PCLStLa-3	3.00	86.33	11.43	25.10	63.47	13.65	25.55	1.87
PCLStLa-4	4.00	90.80	6.23	21.27	72.50	14.70	26.68	1.81

*Calculated from ^{1}H NMR. St: 1.39 g; PCL-Br: 1.00 g

Table 4. The impact of polymerization time on one-pot block copolymerization

Code	PCL-Br (g)	LA (g)	St (g)	Time (h)	Yield (wt%)	Mn,GPC (kDa)	Mw,GPC (kDa)	PDI
PCLLaSt-T1	1.00	1.00	2.08	1	41.67	8.17	13.35	1.63
PCLLaSt-T2	1.00	1.00	2.08	3	64.90	9.08	13.88	1.52
PCLLaSt-T3	1.00	1.00	2.08	5	85.30	13.44	21.39	1.59
PCLLaSt-T4	1.00	1.00	2.08	8	89.10	14.71	24.57	1.67
PCLLaSt-T5	1.00	1.00	2.08	15	92.10	14.95	25.30	1.69
PCLLaSt-T6	1.00	1.00	2.08	21	96.47	15.75	28.86	1.83
PCLLaSt-T7	1.00	1.00	2.08	24	98.30	15.94	29.39	1.84

The impact of polymerization time on copolymerization were investigated using simultaneous ring-opening polymerization and atom transfer radical polymerization processes. The impact of polymerization time on one-pot block polymerization is shown in Table 4. Polymers with a higher molar mass are obtained from polymerizations that last longer.

As shown in Figure 2, the molecular weight (Mn) values of the PLA-b-PCL-b-PSt block copolymers were determined by GPC. The polydispersity values of block copolymers are in the range of 1.47-1.87, according to GPC data. Since the polymerization is initiated by more than one propagating core, the polydispersity values of block copolymers are comparatively higher than anticipated. Since the ROP catalyst Sn(Oct)$_2$ of D, L-lactide could intervene with the radical polymerization of St, block copolymers with relatively narrow molecular weights distributions can be produced. The GPC curves of all polymers were unimodal and observed that the molecular weight values of PLA-b-PCL-b-PSt block copolymers are much higher than the PCL-Br macroinitiator. For example, the unimodal GPC curves of the block copolymers are shown in Figure 2.

^{1}H NMR spectroscopy was used to characterize PCL-b-PSt and PLA-b-PCL-b-PSt block copolymer samples. Figure 3 shows typical ^{1}H NMR spectra of PCL-b-PSt and PLA-b-PCL-b-PSt (PCLSt-La-2) block copolymer samples. The block copolymer samples' ^{1}H NMR spectra showed characteristic peaks of the associated units: (δ, ppm): 5.1-5.3 ppm (–C**H**–O– in PLA); (δ, ppm): 4.05-4.1 ppm (–C**H**$_2$–O in PCL; (δ, ppm): 6.4–7.1 ppm (-C$_6$**H**$_5$ in PSt). The peak areas of the (–C**H**–) protons in the PLA units (5.1-5.3 ppm), phenyl protons in PSt (6.4–7.1 ppm), and (–C**H**$_2$–O–) protons in PCL units (4.05-4.1 ppm) were measured using ^{1}H NMR to determine the PLA, PCL, and PSt contents in mol per cent (given in Tables 1, 2, 3).

Figure 4 (a) shows the FTIR spectrum of PCL-Br macroinitiator the stretching vibration peak of aliphatic -C-H, C=O, and -C-O (ether linkage) in the PCL molecular chain could be due to the high absorption peak at 2920, 1732, and 1110 cm^{-1}, respectively. Figure 4 (b) shows the FTIR spectrum of the PLA-b-PCL-b-PSt block copolymer (PCLStLa-2). The position of the C=O absorption peak is the main difference between Figures 4 (b) and (a). The C=O absorption peak expands and divided into two peaks, where the vigorous absorption peak at 1758 cm^{-1} can be attributed to C=O on the PLA segment in the copolymer in Figure 4 (b). The absorption peaks at 3020 and 1600 cm^{-1} on the PSt segment of the copolymer can be attributed to the aromatic -C-H and phenyl -C-H absorption peaks, respectively, as shown in Figure 4 (b). These findings indicate that the PLA ve PSt chain is present in the synthesized copolymer.

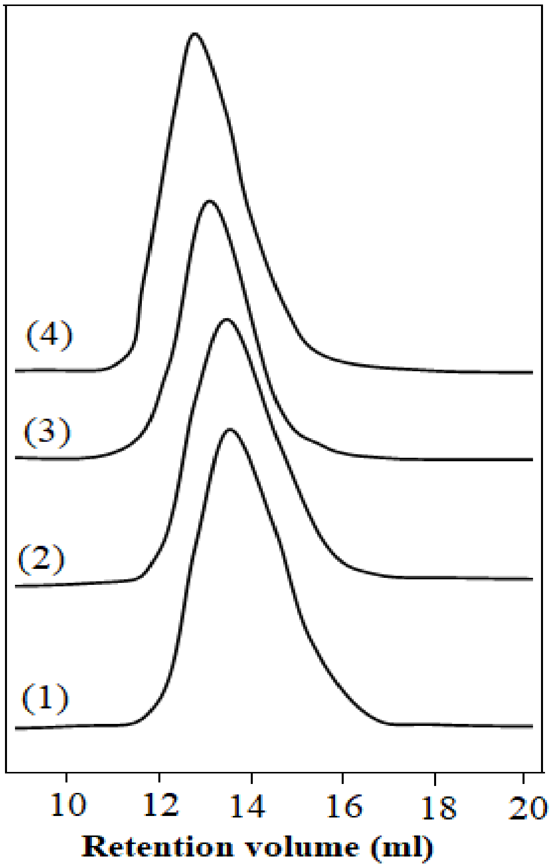


Figure 2. GPC curves of PLA-b-PCL-b-PSt block copolymers [PCLLaSt series in (Table 1)]

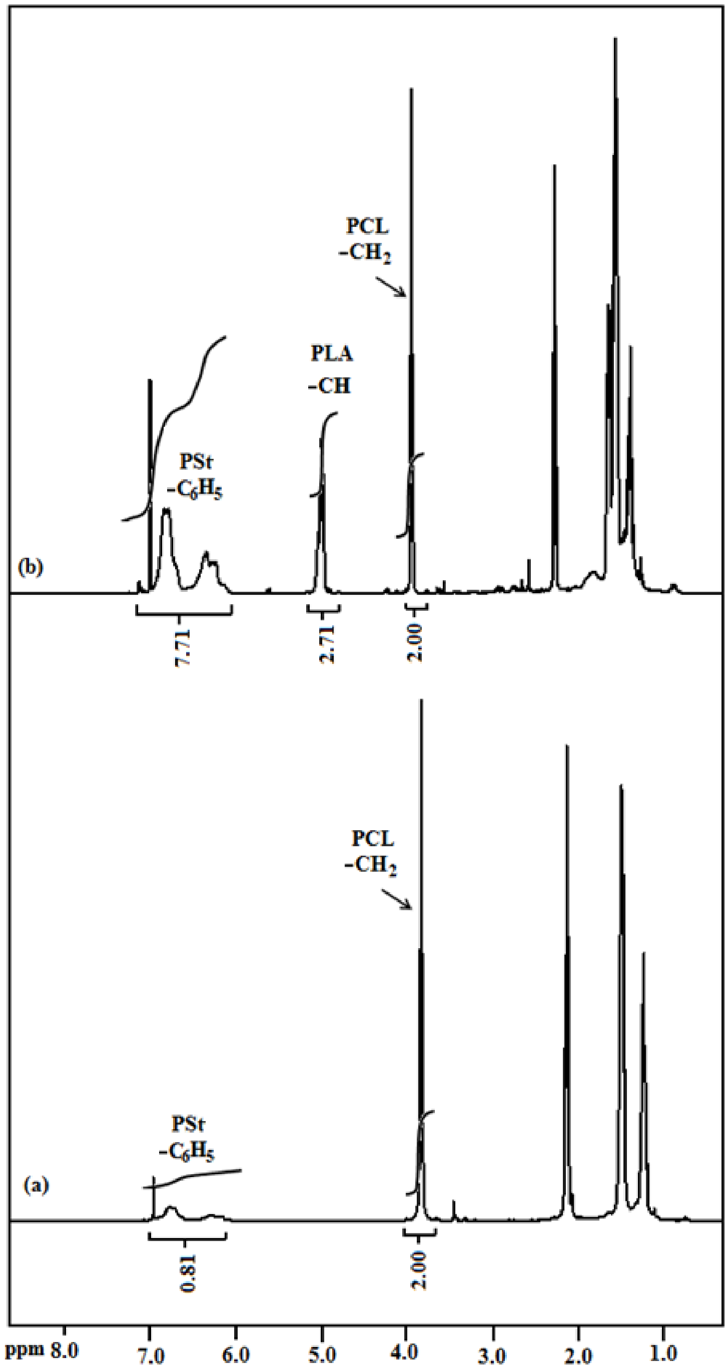


Figure 3. ^{1}H NMR spectra of (a) PCL-b-PSt block copolymer (PCLSt); (b) PLA-b-PCL-b-PSt block copolymer (PCLStLa-2)

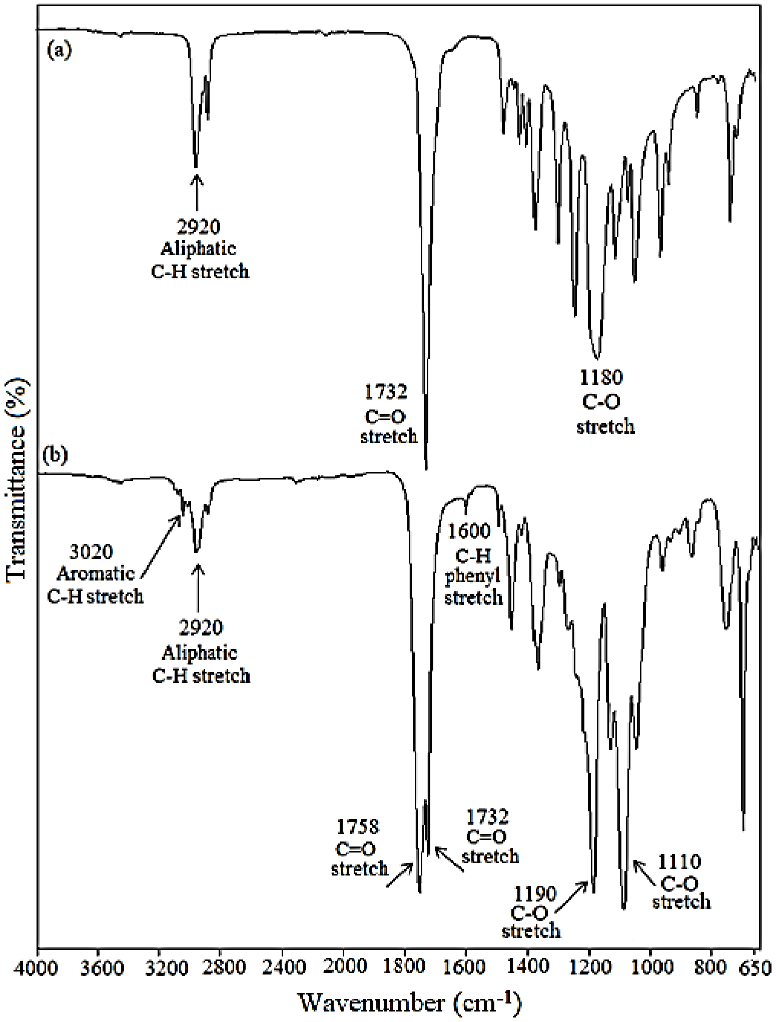


Figure 4. FTIR spectrum of (a) PCL-Br macroinitiator; (b) PLA-b-PCL-b-PSt block copolymer (PCLStLa-2)

CONCLUSION

The block copolymer was synthesized in one-pot using the PCL-Br macroinitiator ATRP of styrene (St) and ROP of D, L-lactide (LA). The PCL-Br macroinitiator demonstrated typical initiator action in the copolymerization of St and LA. PLA-b-PCL-b-PSt block copolymers were evaluated using one-pot synthesis, ATRP, and ROP conditions. The block copolymer was obtained with a relatively high molecular weight. The proposed method is straightforward and efficient for preparing block copolymers. This study demonstrated that the materials produced by the synergistic combination of PLA, PCL, and PSt can be used in areas with wide technological application potential.

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Conflict of Interest

The article author declare that there is no conflict of interest.

Author’s Contributions

I hereby declare that the planning, execution, and writing of the article were done by me as the sole author of the article.

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